Spin-Selective Correlation Experiment for Measurement of Long-Range
J Couplings and for Assignment of (R/S) Enantiomers from the Residual
Dipolar Couplings and DFT

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## 1. C-HETSERF spectrum of the Cyclosporine $A$ :

The 800 MHz 2D C-HETSERF spectrum of cyclosporine A. Eight scans are accumulated for each one of the $200 t_{1}$ increments and the number of the data points in $t_{2}$ was set to 4608 . The spectral widths in both dimensions were 7700 Hz . Prior to Fourier transformation, zero filling to 4 K in $\mathrm{F}_{1}$ and 16 K points in $\mathrm{F}_{2}$ and sine squared window function in both dimensions were applied. The recycle delay was set to 3.5 s


## 2. C-HETSERF spectrum of the $(R / S)$-propylene carbonate :

The 2D C-HETSERF spectrum of (R/S)-propylene carbonate in $\mathrm{PBLG}^{2} \mathrm{CDCl}_{3}$ solvent was recorded at 300 K . The delay $\Delta$ was 1.8 ms . The flip angle used was $26^{\circ}$. Eight scans were accumulated for each of the $512 t_{1}$ increments and the number of the data points in $t_{2}$ was set to 8332. The spectral widths in both the $\mathrm{F}_{2}$ and $\mathrm{F}_{1}$ dimensions are 2000 Hz . Zero filling to 2048 in $\mathrm{F}_{1}$ and 8192 points in $\mathrm{F}_{2}$ and sine squared window function in both dimensions were applied before processing. The recycle delay was set to 3 s . The eleven couplings used within the PALES program are given by the separations "a-i".



The separations "a-i" represent the couplings $a={ }^{3} T_{\mathrm{C} 1 \mathrm{H} 6}, b={ }^{3} \mathrm{~T}_{\mathrm{ClH7} 7}, \mathrm{c}^{2} \mathrm{~T}_{\mathrm{C} 1 \mathrm{H} 5, ~} \mathrm{~d}^{1} \mathrm{~T}_{\mathrm{C} 3 \mathrm{H} 6}, \mathrm{e}={ }^{1} \mathrm{~T}_{\mathrm{C} 3 \mathrm{H} 7}$, $f={ }^{1} T_{\mathrm{C} 2 \mathrm{H} 5}, g={ }^{2} \mathrm{~T}_{\mathrm{C} 2 \mathrm{H} 6}, \mathrm{~h}==^{2} \mathrm{~T}_{\mathrm{C} 2 \mathrm{H} 7,}, \mathrm{i}^{2} \mathrm{~T}_{\mathrm{C} 3 \mathrm{H} 5}$, respectively for both the enantiomers. The magnitudes of couplings are given in the text.

## 3. INADEQUATE experiment of the (R/S)-propylene carbonate :

All the two-dimensional ${ }^{13} \mathrm{C}^{13} \mathrm{C}$ INADEQUATE spectra were recorded on an 800 MHz spectrometer at 300 K using a recycle delay time of 3 sec . The spectral widths of 24 K Hz in $\mathrm{F}_{1}$ and 12 K Hz in $\mathrm{F}_{2}$ were used. 128 scans are accumulated for each of the $96 \mathrm{t}_{1}$ increments and the number of the data points in $t_{2}$ was set to 776 . Prior to Fourier transformation, zero filling to 512 in $F_{1}$ and 2 K points in $\mathrm{F}_{2}$ and sine squared window function in both dimensions were applied. The recycle delay was set to 4 s .

Traces from the two-dimensional ${ }^{13} \mathrm{C}-{ }^{13} \mathrm{C}$ INADEQUATE experiment of $(R / S)$-propylene carbonate in both PBLG/CDCl3 solvent and $\mathrm{CDCl}_{3}$. The following figures show ${ }^{1} T_{\mathrm{CC}}$ and ${ }^{1} J_{\mathrm{CC}}$.



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## 4. Alignment tensor elements

The alignment tensor for the $R$-propylene carbonate in $\mathrm{PBLG} / \mathrm{CDCl}_{3}$ liquid crystalline phase. Below are the values of the alignment tensor for the RDCs of set-I fitted to $R$-structure.

| n (RDC) | 8 | 11 |
| :--- | :---: | :---: |
| Da/ Hz | $-3.45 \times 10^{-3}$ | $-3.08 \times 10^{-3}$ |
| DaNH / Hz | -37.3 | -33.3 |
| R | 0.39 | 0.37 |
| Axx | $7.15 \times 10^{-4}$ | $6.70 \times 10^{-4}$ |
| Ayy | $2.74 \times 10^{-3}$ | $2.41 \times 10^{-3}$ |
| Azz | $-3.45 \times 10^{-3}$ | $-3.08 \times 10^{-3}$ |
| EV Axx | $-0.03 ;-0.34 ; 0.93$ | $-0.01 ;-0.35 ; 0.93$ |
| EV Ayy | $0.78 ;-0.58 ;-0.18$ | $0.78 ;-0.58 ;-0.21$ |
| EV Azz | $0.61 ; 0.73 ; 0.29$ | $0.62 ; 0.72 ; 0.27$ |
| RMSD | 2.409 | 3.781 |
| CORR | 0.995 | 0.988 |

Da: axial component of alignment tensor and DaNH : axial component of the alignment tensor normalized to NH vectors

R: rhombicity
Axx, Ayy, Azz: main axes of the alignment tensor
EV Axx, EV Ayy, EV Azz : Eigenvectors for the corresponding main axes of the tensor $n(R D C)$ : number of RDCs used for the calculation of the parameters with PALES.
5. Table 1. The experimental and back-calculated RDCs obtained using the optimized structure of $R$ within the PALES.

| Coupling | Set-I |  | Set-II |  |
| :---: | :---: | :---: | :---: | :---: |
|  | Experimental | ${ }^{\text {a }}$ Theoretical | Experimental | ${ }^{\mathrm{b}}$ Theoretical |
| C1H5 | 2.0 | -7.6 | 2.9 | -7.3 |
| C1H7 | 3.7 | -5.7 | 3.3 | -7.2 |
| C1H6 | 2.3 | -5.4 | 2.7 | -6.1 |
| C2H5 | 27.7 | 27.5 | 26.3 | 26.5 |
| C2H7 | 1.9 | 1.0 | 0.00 | -1.9 |
| C2H6 | 2.0 | -7.3 | 1.9 | -9.9 |
| C3H5 | 2.5 | 0.3 | 3.1 | -2.7 |
| C3H6 | 23.5 | 24.8 | 30.0 | 31.4 |
| C3H7 | 14.5 | 15.5 | 9.4 | 10.8 |
| C1C2 | -9.8 | -8.9 | -9.2 | -8.4 |
| C2C3 | -7.7 | -6.2 | -10.7 | -8.8 |

${ }^{\text {a }}$ theoretical RDCs when the eleven RDCs of Set-I are used
${ }^{\mathrm{b}}$ theoretical RDCs when the eleven RDCs of Set-II are used.
6. Table 2. Tabulation of the each of experimental and back-calculated RDCs derived using the optimized structure of $S$ enantiomer using the PALES.

| Coupling | Set-I |  | Set-II |  |
| :---: | :---: | :---: | :---: | :---: |
|  | Experimental | ${ }^{\text {a }}$ Theoretical | Experimental | ${ }^{\mathrm{b}}$ Theoretical |
| C2H5 | 27.7 | 27.0 | 26.3 | 25.5 |
| C2H7 | 1.9 | -8.6 | 0.00 | 0.5 |
| C2H6 | 2.0 | -7.7 | 1.9 | -1.9 |
| C3H5 | 2.5 | -0.6 | 3.1 | 2.6 |
| C3H6 | 23.5 | 25.3 | 30.0 | 30.8 |
| C3H7 | 14.5 | 15.4 | 9.4 | 10.2 |
| C1C2 | -9.9 | -6.8 | -9.2 | -9.4 |
| C2C3 | -7.7 | -9.8 | -10.7 | -9.6 |

${ }^{\text {a }}$ theoretical RDCs when the eight RDCs of Set-I were used. ${ }^{\text {b }}$ theoretical RDCs when the eight RDCs of Set-II were used.
7. Additional confirmation using SERF spectrum of $(R / S)$-propylene carbonate :


The SERF experiment for $(R / S)$-propylene carbonate was recorded and presented above. From the SERF spectrum, the outer triplet in the indirect dimension could be assigned to the $R$ enantiomer whereas inner one for the $S$ enantiomer as the sample is $R$ enriched. Looking at intensities of different cross sections, peaks can be assigned unambiguously for $R$ enantiomer in the direct dimension. The direct dimension represents the one dimensional proton spectrum of the methyl region. With the help of this information, the whole 2 D spectrum could be assigned. The assignments obtained by this method are exactly same as what is described in this article. This further vindicates the applicability of the present method.

